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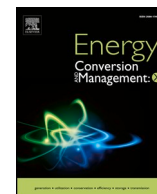
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Prediction and optimisation of syngas production from air gasification of Napier grass via stoichiometric equilibrium model

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ABSTRACT

Napier grass is a promising candidate as a potential solid biofuel due to its wide availability, high growth rate, carbon neutrality and high volatility. Syngas is produced from gasification of Napier grass which can be further utilised for production of renewable fuel and other chemicals. The quality of the syngas produced from gasification of Napier grass is dependent on various factors such as operating temperature and pressure, gasification medium, biomass versus air ratio and moisture content. The optimisation of process parameters is important due to productivity and economic reasons. Experimental investigations to determine optimum conditions for gasification process are cost intensive and time consuming, rendering these techniques to be impractical. Thus, in this study, a stoichiometric equilibrium model for simulation of air gasification of Napier grass is developed. The model is modified to include correction factors at a series of temperatures and ERs which are multiplied with equilibrium constants to improve the accuracy of the model in predicting syngas and carbon compositions. The predicted values are in good agreement with experimental measurement, validating the model as a reliable tool for simulation of gasification performance. The modified model is further utilised to determine optimum operating conditions for maximum hydrogen production.

1. Introduction

Biomass gasification is one of the promising thermochemical processes that transforms solid biomass into syngas, biochar, ash, tars, and oils. The syngas generated can be used for fuel production such as H₂, CH₄, biodiesel, and also for manufacturing of many chemicals such as ammonia, urea, ethanol and others. Among other thermochemical conversion processes, gasification is a flexible technology for processing of various biomass resources into renewable fuel and other chemicals with a good potential for commercial expansion in Malaysia due to the wide availability of biomass in the country [1]. The reactions involved in gasification is complex in nature and the outputs of the process are affected by various factors such as operating parameters (temperature, pressure, air to biomass ratio etc) and biomass feedstock characteristics (moisture content, proximate composition etc) [2]. The understanding

of the effects of each operating parameter on the performance of the gasification system can be achieved through experimental work which is time consuming and resource intensive. To overcome the limitations posed by experimental investigations, mathematical models for gasification process have been developed to decipher the complexity of gasification reactions. The models serve as important tools for prediction of gasification outputs and can be further utilised for process optimisation to achieve the desired syngas composition without repetitive experimental investigations.

There are various approaches for modelling of gasification such as kinetic modelling, computational fluid dynamics (CFD), thermodynamic equilibrium model, artificial neural network (ANN) and many others found in the literatures [3]. In addition, thermodynamic equilibrium modelling can be further classified into stoichiometric and non-stoichiometric equilibrium approaches. Stoichiometric equilibrium

Abbreviations: ANN, Artificial neural network; CFD, Computational fluid dynamics; ER, Equivalence ratio; GC, Gas chromatography; NG, Napier grass; RMS, Root mean square

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Nomenclature

a	Number of atom of carbon in the feedstock fuel	n_4	Number of moles of H_2O
b	Number of atom of hydrogen in the feedstock fuel	n_5	Number of moles of CH_4
c	Number of atom of oxygen in the feedstock fuel	n_6	Number of moles of N_2
C	Number of components	n_7	Number of moles of solid carbon
d	Number of atom of nitrogen in the feedstock fuel	n_8	Number of moles of hydrocarbon
D_p	Diameter of sand particle (bed material)	p	Number of nitrogen atoms in hydrocarbon
ER	Equivalence ratio	P	Number of phases
F	Degree of freedom	Re_{mf}	Reynolds number at minimum fluidisation velocity
f_i	Molar flow rate of NG feedstock fuel	T	Temperature
g	Acceleration due to gravity	U_{mf}	Minimum fluidisation velocity
h	Stoichiometric coefficients of oxygen per mole of biomass feedstock in gasification reaction	w	Stoichiometric coefficients of moisture per mole of biomass feedstock in gasification reaction
k_{CO_2}	Thermodynamic equilibrium constant for formation reaction of CO_2	x	Number of carbon atoms in hydrocarbon
k_{H_2O}	Thermodynamic equilibrium constant for formation reaction of H_2O	y	Number of hydrogen atoms in hydrocarbon
k_{CH_4}	Thermodynamic equilibrium constant for formation reaction of CH_4	z	Number of oxygen atoms in hydrocarbon
k_{CO}	Thermodynamic equilibrium constant for formation reaction of CO	α_1	Correction factor of methane decomposition reaction at different ER
K_{HWGS}	Equilibrium constant for heterogeneous water-gas shift reaction	α_2	Correction factor of water-gas shift reaction at different ER
K_{MD}	Equilibrium constant for methane decomposition reaction	α_3	Correction factor of heterogeneous water-gas shift reaction at different ER
K_{WGS}	Equilibrium constant for water-gas shift reaction	β_1	Correction factor of methane decomposition reaction at different temperature
M	Moisture content per mol of NG	β_2	Correction factor of water-gas shift reaction at different temperature
n_1	Number of moles of H_2	β_2	Correction factor of heterogeneous water-gas shift reaction at different temperature
n_2	Number of moles of CO	μ	Viscosity of fluid media
n_3	Number of moles of CO_2	ρ_{air}	Density of fluidising media (air)
		ρ_p	Density of bed material

approach is based on the calculation of equilibrium constant for common chemical reactions that involve in the gasification process such as methane decomposition, water-gas shift and heterogeneous water-gas shift reactions [4]. Meanwhile, in a non-stoichiometric methodology, the strategy is focused on minimisation of Gibbs free energy for gasification process. Kinetic modelling approach involves calculation of both kinetic and hydrodynamics of reactions inside the gasifier reactor [3].

In recent years, the works pertaining to gasification modelling via stoichiometric equilibrium approach have been focussing on the inclusion of correction factors to modify the equilibrium constant in each reaction based on the experimental data. The action improves the accuracy of the model in predicting composition of syngas produced from gasification of any given biomass feedstock at specified operating conditions [5–7]. Li, Grace [8] reported that stoichiometric equilibrium model is able to determine the maximum potential biomass conversion according to the equilibrium limit and the information is useful for process design, evaluation and improvement. In addition, Huang and Ramaswamy [6] stated that stoichiometric equilibrium model is a simple tool for predicting the performance of gasifier for preliminary techno-economic analysis. However, the works conducted previously are confined to singular fixed process parameter which is the gasification temperature. To expand the practicality of stoichiometric equilibrium model, Ng, Ng [9] developed a numerical model for gasification of palm-based biomass that integrates the operating temperature of the gasifier. The model was further expanded to simulate gasification of a range of different biomasses which are bagasse, rice husk and coconut shell [10].

Most of the works related to stoichiometric equilibrium modelling of gasification process concentrated on operating temperature while other operating conditions are kept constant and not studied extensively. According to the findings reported in literature [11–13], in addition to gasification temperature, other operating parameters such

as type of gasification agent, biomass versus gasification agent ratio, pressure and so on have significant effects on composition of syngas produced from the process. Therefore, other process parameters should be analysed and included into the model to improve the accuracy of the model in predicting syngas composition. In this work, gasification of Napier grass is simulated using stoichiometric equilibrium. The model is expanded to simulate the process at varying gasification temperature and biomass versus air ratio (ER). The proposed model includes correction factors into the equilibrium constants as functions of both temperatures and biomass versus air ratio. The findings from modelling work are validated against experimental results. The validated model is then further utilised for optimisation of hydrogen production. Napier grass, which is also known as *Pennisetum purpureum* is chosen as biomass feedstock in this study due to its wide availability, high growth rates, carbon neutrality and high volatility. The rapid rate of NG growth produces a high biomass yield which is 40 tonnes per hectare per annum [14]. The rate is equivalent to 100 barrels of oil equivalent per hectare [15]. NG can be harvested up to four times per year and the ratio of energy output to energy input is reported to be 25:1 [16]. Despite various advantages offered by NG, there are limited studies are

Table 1
Proximate and ultimate analyses of Napier grass.

Proximate Analysis (wt% dry basis)	
Volatile matter	85.57
Fixed carbon	8.17
Ash content	6.31
Ultimate Analysis (wt% dry basis)	
Carbon	45.10
Hydrogen	5.94
Nitrogen	0.45
Sulphur	0
Oxygen	48.52

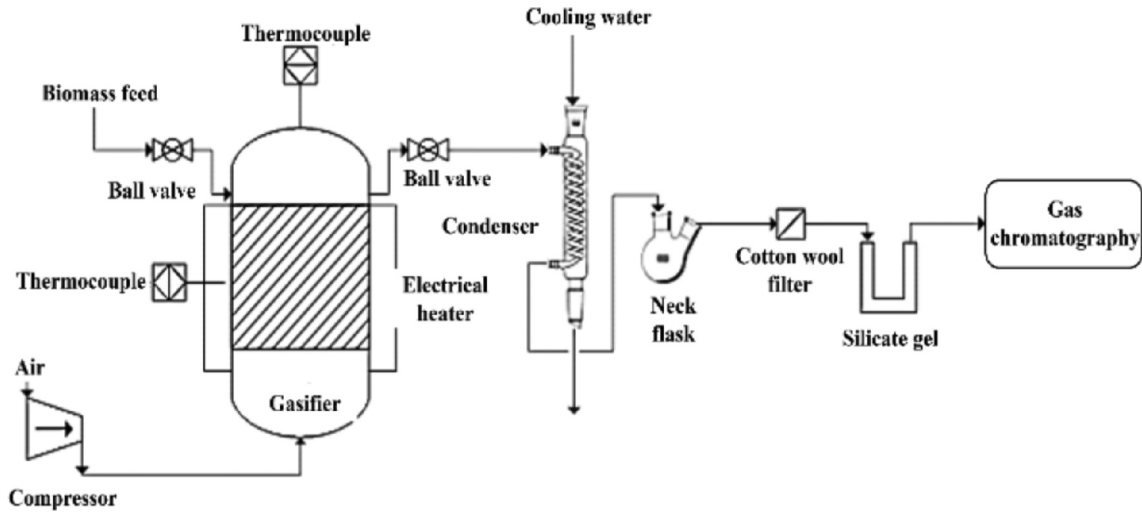


Fig. 1. Schematic diagram of lab scale updraft fluidised bed reactor.

Table 2

The operating conditions for gasification tests.

Pressure (P), kPa	Bed temperature (T), °C	Biomass flow rate (kg/h)	Superficial gas velocity (U), Nm/s	ER
101.325	650–850	0.167	0.017 – 0.035	0.20 – 0.40

Table 3

Properties of bed material.

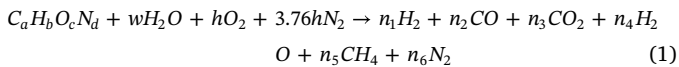
Bed materials	Geldart group	ρ (kg/m ³)	Particle size, dp (μ m)
Sand	Group B (sand like) [24]	2650 [25,26]	90–125

reported regarding the use of NG as an energy feedstock for power generation via gasification technology.

2. Methodology

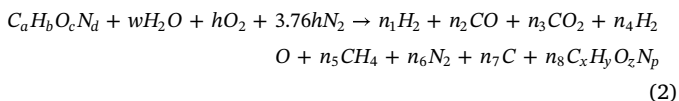
2.1. Gasification stoichiometric equilibrium approach

The general chemical formula of a dry biomass fuel is defined as $C_aH_bO_cN_d$ where the composition can be determined from ultimate analysis of the biomass. Zainal, Ali [17] have developed a global gasification reaction of biomass with air (79% of N_2 and 21% of O_2) and the equation is written as in Eq. (1).



where a, b, c, and d is the number of atoms of carbon, hydrogen, oxygen and nitrogen in the feedstock fuel; n_1 – n_6 is the number of moles of H_2 , CO , CO_2 , H_2O , CH_4 and N_2 ; w and h are the stoichiometric coefficients (per mole of biomass feedstock) of moisture and oxygen respectively.

Based on the gasification experiment conducted, a significant amount of hydrocarbon and solid carbon were generated throughout the process. Thus, the gasification reaction developed by Zainal, Ali [17] is modified to include hydrocarbon ($C_xH_yO_zN_p$) and solid carbon (C). The modified global gasification reaction is written as in Eq. (2).



where x, y, z and p represent the number of atoms of C, H, O and N in the hydrocarbon; n_7 and n_8 are the number of moles of solid carbon (C) and hydrocarbon ($C_xH_yO_zN_p$).

Based on Eq. (2), the atomic balances of each component (C, H, O and N) for the gasification model are expressed as follow.

$$C: af_i = n_2 + n_3 + n_5 + n_7 + xn_8 \quad (3)$$

$$H: bf_i + 2w = 2n_1 + 2n_4 + 4n_5 + yn_8 \quad (4)$$

$$O: cf_i + w + 2h = n_2 + 2n_3 + n_4 + zn_8 \quad (5)$$

$$N: df_i + 2(3.76)h = 2n_6 + pn_8 \quad (6)$$

where f_i is the molar flow rate of NG feedstock fuel.

In this modelling work, the enthalpy balance is neglected as the additional heat transferred into the gasifier is not considered. Therefore, only mass balance and thermodynamic equilibrium equations are taken into account. Since the gasifier is operated at high temperature but maintained at atmospheric pressure, the syngas can be assumed as an ideal gas, whereas ash and N_2 are assumed as inert at high temperature. The operation of the gasifier is assumed to be under steady state and ambient pressure.

According to Ng, Tay [10], there are five main gasification reactions that involve all product gas components and carbon, which are Boudouard equilibrium, methane decomposition and heterogeneous water-gas shift reaction, hydrogenating gasification and water-gas shift reactions which are listed below.

Boudouard Equilibrium



Hydrogenating Gasification



Methane Decomposition



Water-Gas Shift



Heterogeneous Water-Gas Shift



In this work, by-product char or ash (solid carbon) is taken into

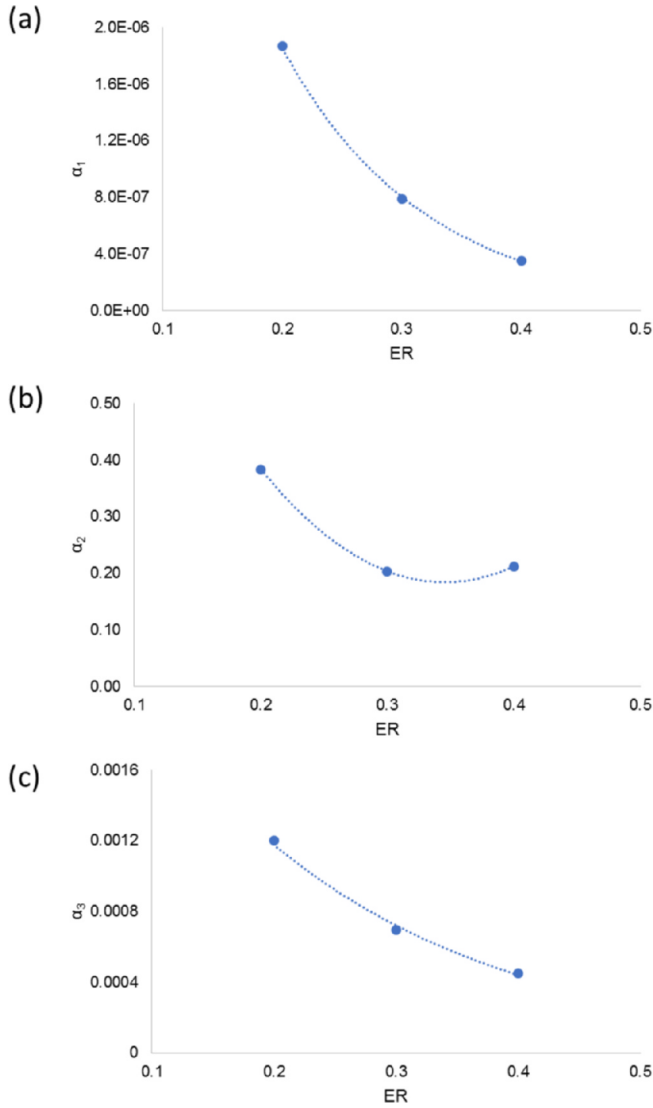


Fig. 2. The relationships between correction factors (a) α_1 (b) α_2 (c) α_3 with ER of NG gasification.

consideration because significant amount of solid component remains unconverted under current gasification conditions. Based on degree of freedom analysis, three independent equilibrium reactions (methane decomposition, water-gas shift reaction and heterogeneous water-gas shift reaction) are needed and selected to represent the interaction of all chemical species.

In the actual gasification process, the reactions might not interact ideally due to the kinetic limitation [18]. Thus, to improve the accuracy of the model in predicting chemical species, the model is modified to include correction factors (α_1 , α_2 , α_3 , β_1 , β_2 , β_3) into the equilibrium constants (K_{MD} , K_{WGS} , K_{HWGS}) [5–7,9,10]. The modified equilibrium constants as functions of number of mole of chemical species are shown below.

$$\alpha_1 K_{MD} = \frac{n_1^3 n_2}{n_4 n_5} P^2 \quad (12)$$

$$\alpha_2 K_{WGS} = \frac{n_1 n_3}{n_2 n_4} \quad (13)$$

$$\alpha_3 K_{HWGS} = \frac{n_1 n_2}{n_4} P \quad (14)$$

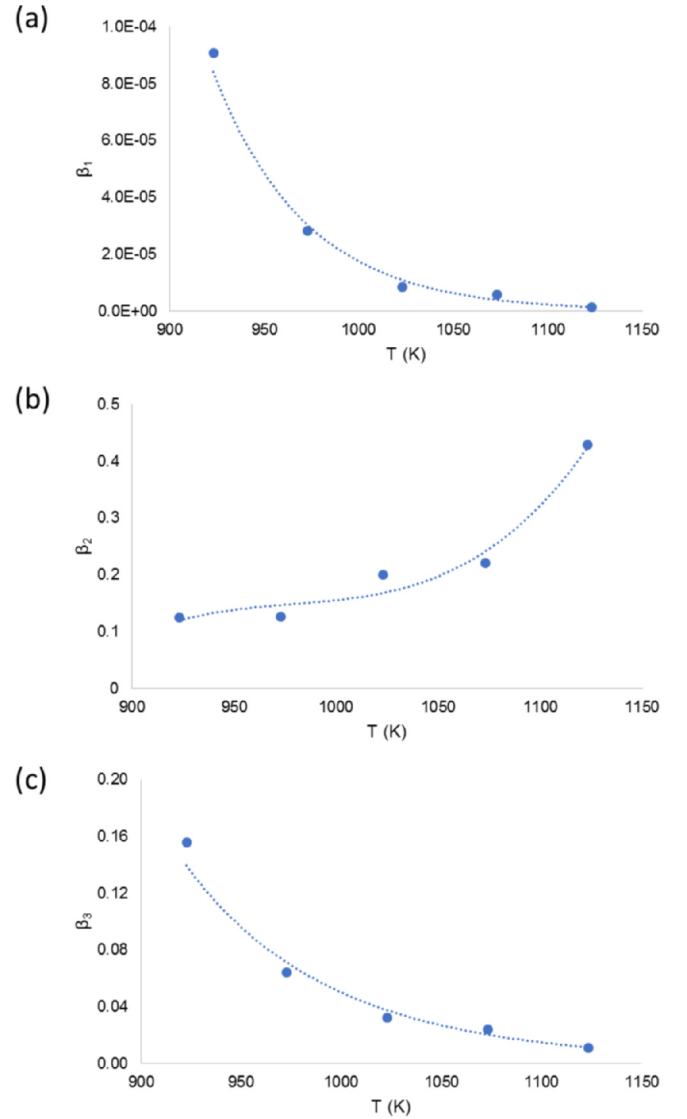


Fig. 3. The relationships between correction factors (a) β_1 (b) β_2 (c) β_3 with gasification temperature of NG.

$$\beta_1 K_{MD} = \frac{n_1^3 n_2}{n_4 n_5} P^2 \quad (15)$$

$$\beta_2 K_{WGS} = \frac{n_1 n_3}{n_2 n_4} \quad (16)$$

$$\beta_3 K_{HWGS} = \frac{n_1 n_2}{n_4} P \quad (17)$$

where K_{MD} , K_{WGS} , and K_{HWGS} are equilibrium constants for three independent reactions which are methane decomposition, water-gas shift and heterogeneous water-gas shift reactions respectively, $n_1 - n_5$ are number of moles of gas species (H_2 , CO , CO_2 , H_2O , CH_4) and P is ambient pressure.

The relationship between equilibrium constants and thermodynamic equilibrium constants are shown below.

$$K_{MD} = \exp(k_{CO} - k_{H_2O} - k_{CH_4}) \quad (18)$$

$$K_{WGS} = \exp(k_{CO_2} - k_{H_2O} - k_{CO}) \quad (19)$$

$$K_{HWGS} = \exp(k_{CO} - k_{H_2O}) \quad (20)$$

where k_{H_2O} , k_{CH_4} , k_{CO} , and k_{CO_2} are the thermodynamic equilibrium constants for the formation reaction of H_2O , CH_4 , CO and CO_2 at

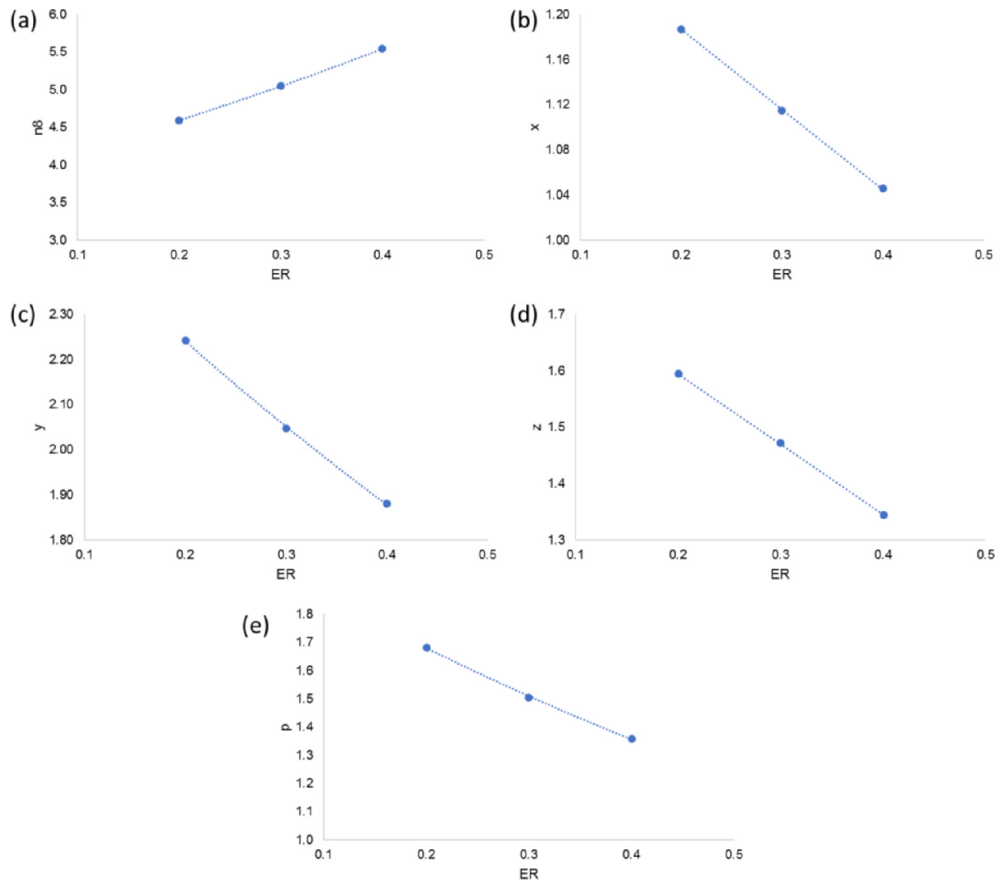


Fig. 4. Change of (a) n_8 , (b) x , (c) y , (d) z , (e) p at a series of ER.

operating temperature T .

According to Baron et al. [19], k_{H_2O} , k_{CH_4} , k_{CO} and k_{CO_2} can be presented by the following equations.

$$\ln k_{H_2O} = 28,780 T^{-1} - 0.69477 \ln T - 1.4283 \times 10^{-3} T + 0.74925 \times 10^{-6} T^2 - 1.3785 \times 10^{-10} T^3 \quad (21)$$

$$\ln k_{CH_4} = 8372.2 T^{-1} - 1.0769 \ln T - 5.6435 \times 10^{-3} T + 2.9046 \times 10^{-6} T^2 - 5.2351 \times 10^{-10} T^3 \quad (22)$$

$$\ln k_{CO} = 13612 T^{-1} + 1.8317 \ln T - 2.7584 \times 10^{-3} T + 0.6536 \times 10^{-6} T^2 - 0.78772 \times 10^{-10} T^3 \quad (23)$$

$$\ln k_{CO_2} = 47,280 T^{-1} + 0.1322 \ln T - 0.94025 \times 10^{-3} T + 0.45112 \times 10^{-6} T^2 - 0.91901 \times 10^{-10} T^3 \quad (24)$$

The modified models are used to predict syngas composition at a series of operating temperature and ER. The root mean square (RMS) method is used to evaluate the deviation between the predicted and experimentally measured gas composition produced from gasification of NG. RMS equation is presented below.

$$RMS = \sqrt{\frac{\sum_g^G (Exp_g - Mod_g)^2}{D}} \quad (25)$$

Where g is producer gas species and carbon, $g \in G$ (H_2 , CO , CO_2 , H_2O , CH_4 , N_2 and C), Exp_g is the experimental results of component g , Mod_g is the predicted results from the model of component g , and D

denotes the number of producer gas species and carbon considered in determining RMS.

2.2. Gasification modelling

In this work, input parameters for modelling of gasification such as ER, temperature, molar flow rate of biomass, biomass moisture content and air are based on actual value from experimental work. By solving the presented model, the composition of syngas can be predicted. In order to determine the unknown amount and composition of hydrocarbon (n_8 , x , y , z , and p) and the value of correction factors (α_1 , α_2 , α_3 , β_1 , β_2 , β_3), the experimental results from a series of ERs and temperatures were substituted into the presented model. Once all unknown values are determined for each set of experiment, the correlations between correction factors (α_1 , α_2 , α_3 , β_1 , β_2 , β_3) with temperature and ER were established. Equilibrium constants (K_{MD} , K_{WGS} and K_{HWGS}) are adjusted based on the correlations of correction factors to provide better prediction of final gas products composition. To validate the model as a reliable tool for prediction of syngas composition from gasification of NG, the calculated RMS value must be very minimum. Once the model is validated, it can be used for optimisation and maximising hydrogen proportion in the syngas.

2.3. Experimental gasification of NG

As mentioned earlier, experimental results obtained from NG gasification conducted in this work are used to validate the developed model. This experiment was conducted at a series of ER (0.2 – 0.4) and operating temperature (923 – 1123 K). Information pertaining to detailed characterisation of Napier grass feedstock and gasification products and by-products is available in [20] and shown in Table 1. Based on the ultimate and proximate analyses, the empirical formula of NG is

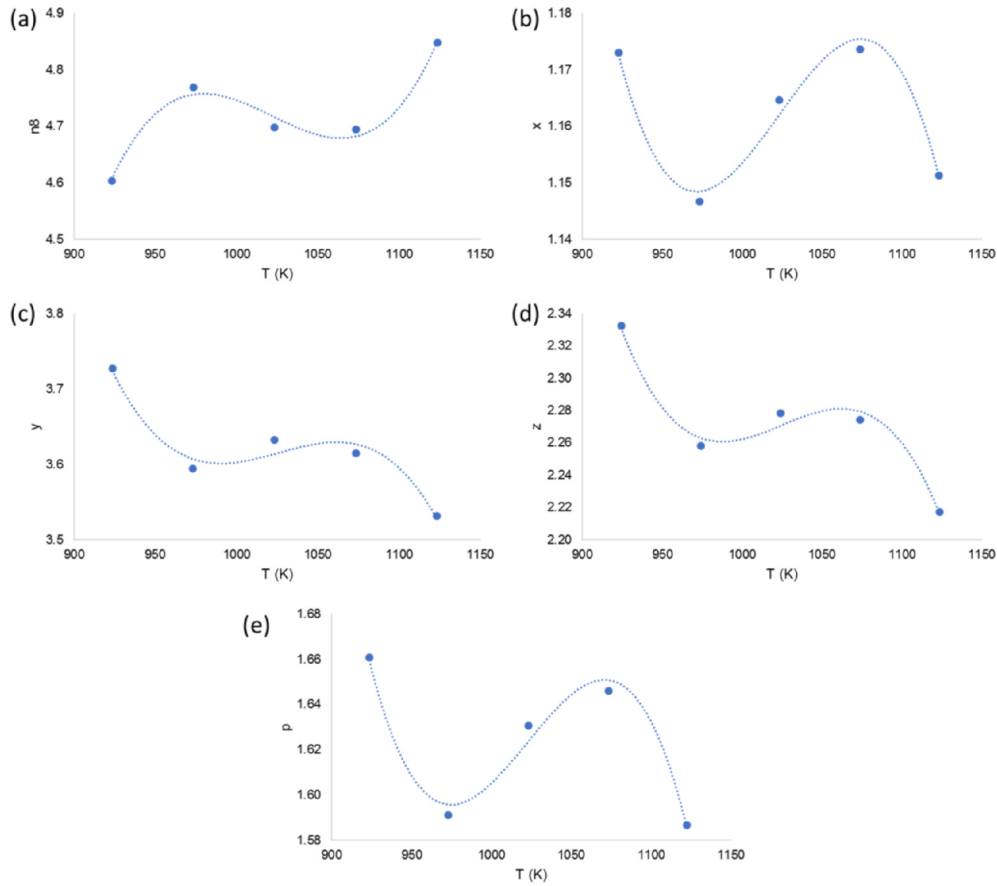


Fig. 5. Change of hydrocarbon amount and composition (a) n₈, (b) x, (c) y, (d) z, (e) p at a series of gasification temperature T.

Table 4

Regression analysis for relationships between correction factors and ER (as plotted in Fig. 2).

Equation number	Empirical correlation	Coefficient of determination (R ²)
Eq. (31)	$\hat{I}_{\pm 1} = 10^{-5}e^{-8.369ER}$	0.9997
Eq. (32)	$\hat{I}_{\pm 2} = 0.615e^{-2.944ER}$	1.0000
Eq. (33)	$\hat{I}_{\pm 3} = 9.4286ER^2 - 6.5075ER + 1.3065$	0.9967

Table 5

Regression analysis for relationships between correction factors and temperature (as plotted in Fig. 3).

Equation number	Empirical correlation	Coefficient of determination (R ²)
Eq. (34)	$\beta_1 = 11536e^{-0.02T}$	0.9723
Eq. (35)	$\beta_2 = 8 \times 10^{-8}T^3 - 0.0002T^2 + 0.2159T - 70.348$	0.9699
Eq. (36)	$\beta_3 = 1 \times 10^{36}T^{-12.82}$	0.9769

given as CH_{1.56}O_{0.81}N_{0.0043} with 30.07 wt% of water. In order to determine the stoichiometric coefficient of biomass moisture, w which is required in gasification equation (Eq. (1)), the measured moisture content in biomass need to be converted via Eq. (28), which is derived from Eqs. (26) and (27) [17].

Let M = Moisture content per mol of NG

$$M = \frac{\text{mass of water}}{\text{mass of wet biomass}} \times 100\% \quad (26)$$

Table 6

Regression analysis for relationships between hydrocarbon amount and composition with ER (as plotted in Fig. 4).

Equation number	Empirical correlation	Coefficient of determination (R ²)
Eq. (37)	$n_8 = 3.8069e^{0.9399ER}$	0.9995
Eq. (38)	$x = (-0.7094)ER + 1.3284$	0.9998
Eq. (39)	$y = 2.672e^{-0.88ER}$	0.9997
Eq. (40)	$z = (-1.2595)ER + 1.8486$	0.9999
Eq. (41)	$p = 2.0899e^{-1.088ER}$	0.9997

Table 7

Regression analysis for relationships between hydrocarbon amount and composition with temperature (as plotted in Fig. 5).

Equation number	Empirical correlation	Coefficient of determination (R ²)
Eq. (42)	$n_8 = 3 \times 10^{-7}T^3 - 0.0008T^2 + 0.8322T - 277.66$	0.9827
Eq. (43)	$x = (-5) \times 10^{-8}T^3 + 0.0002T^2 - 0.1586T + 54.979$	0.9777
Eq. (44)	$y = (-8) \times 10^{-8}T^3 + 0.0003T^2 - 0.2577T + 90.513$	0.9688
Eq. (45)	$z = (-6) \times 10^{-8}T^3 + 0.0002T^2 - 0.1888T + 65.953$	0.9837
Eq. (46)	$p = (-1) \times 10^{-7}T^3 + 0.0004T^2 - 0.384T + 131.95$	0.9775

Since the relative molecular weight of water and NG biomass are 18 and 26.58 respectively, then

$$M = \frac{18w}{26.58 + 18w} \times 100\% \quad (27)$$

Therefore,

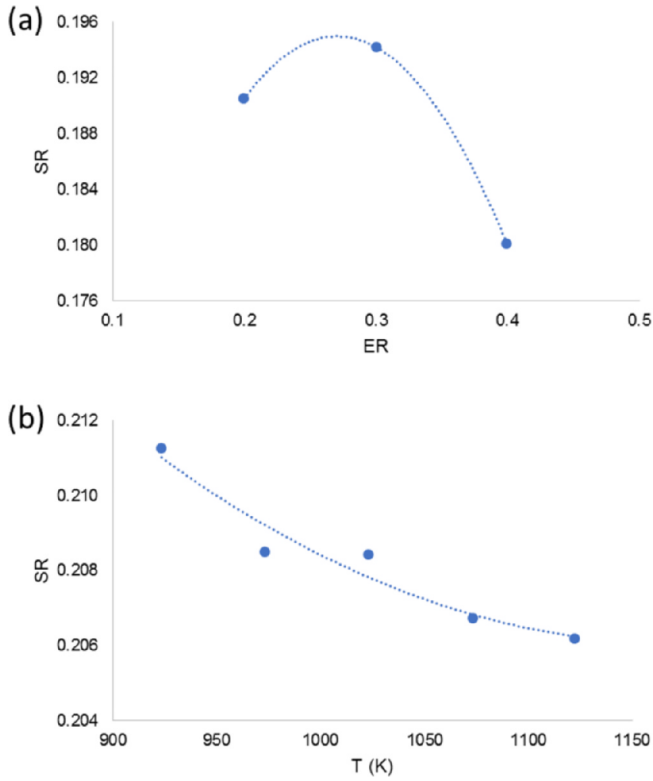


Fig. 6. The relationships between gas to hydrocarbon residues ratio (SR) with (a) ER and (b) temperature.

Table 8

Regression analysis for relationships between gas to hydrocarbon residues ratio (SR) with temperature and ER (as plotted in Fig. 6).

Equation number	Empirical correlation	Coefficient of determination (R^2)
Eq. (47)	$SR = 8E-08 T^2 - 0.0002 T + 0.3172$	0.9384
Eq. (48)	$SR = -0.894ER^2 + 0.4835ER + 0.1296$	1.0000

$$w = \frac{26.68M}{18(1 - M)} \quad (28)$$

2.3.1. Experimental setup

The experimental works were carried out in a gasification system that consists of a heat resistant stainless steel reactor, condenser, gas clean-up unit and gas sampling unit as presented in Fig. 1. The total height and internal diameter of the reactor are 370 mm and 54 mm, respectively. Two individually controlled electric furnaces are used to cover the reactor for heating purpose and preventing the heat loss to atmosphere during operation. Two thermocouples (K-type) were installed, one in the middle of the reactor (gasification zone) and one on top of the reactor (freeboard) to monitor the temperature during experimental operation. During the experiment, air was supplied by external compressor and was introduced into the reactor from the base of the bed through a nozzle. The gas produced from feedstock combustion entered the gas condenser section and flowed to the gas clean up section for dust particle filtration. The clean gas was then collected using gas sampling bag and sent for offline GC analysis.

2.3.2. Experimental procedures

The operating conditions used for gasification of NG are shown in Table 2. The minimum fluidisation velocity in the reactor, U_{mf} was determined by using Eq. (29) [21].

$$U_{mf} = \left(\frac{\mu}{D_p \rho_{air}} \left[33.7^2 + 0.0408 \frac{D_p^3 \rho_{air} (\rho_p - \rho_{air}) g}{\mu^2} \right]^{\frac{1}{2}} - 33.7 \right) \quad (29)$$

where Re_{mf} , D_p , ρ_{air} , ρ_p , g , and μ represent the Reynolds number at minimum fluidisation velocity, diameter of sand particle (bed material), density of fluidising media (air), density of bed material, acceleration due to gravity and viscosity of fluid media, respectively.

The range of air volumetric flowrate for the experiment was 0.017 – 0.035 m³/s. Equivalence ratio (ER) for gasification of NG was determined by using Eq. (30) [22].

$$ER = \frac{\text{Actual mass of air/actual mass of dry biomass}}{\text{Stoichiometric air to biomass ratio}} \quad (30)$$

Before start-up of the experiment, sand which was used as bed material was charged into the reactor at a depth-to-radius ratio of 1:1 [23]. The property of sand is presented in Table 3. Then the electric heater was switched on for 2 h to heat up the reactor. Air was injected from air compressor into the reactor after the desired temperature was achieved. NG feedstock was fed into the reactor when the bed temperature was in steady condition. At the end of each experiment, syngas, bio-liquid and bio-char produced from gasification of NG were collected and analysed. Detailed discussion pertaining to analysis of compounds in bio-liquid and bio-char is available in [20].

2.4. Model modification

In this work, thermodynamic equilibrium model for gasification of NG was developed using Lingo 14.0 with Global solver. This software uses branch-and-bound (B&B) algorithm which is coupled with linearisation in order to get globally optimal solutions to non-linear programming (NLP) [27].

2.4.1. Determination of correction factor

As mentioned previously, correction factors were included in the modelling to improve the accuracy of gas and carbon composition prediction. The correction factors were established based on gasification temperature and ER to extend the applicability of the model in a wider range of conditions which can consequently enable the model to identify optimum temperature and ER [4]. Correction factors (α_1 , α_2 , α_3 , β_1 , β_2 , β_3) and the unknown hydrocarbon composition (n_8 , x , y , z , and p) were determined experimentally. The relationships between correction factors with ER and temperature are presented in Fig. 2 and Fig. 3 respectively. The relationships between hydrocarbon amount and composition with ER and temperature are plotted in Fig. 4 and Fig. 5, respectively.

As illustrated in Figs. 2 and 3, the correction factors (α_1 , α_2 , α_3 , β_1 , β_2 , β_3) for methane decomposition reaction, water-gas shift reaction and heterogeneous water-gas shift reaction are not equal to one. This implies that the actual gasification reactions do not achieve equilibrium which might be due to limitations in kinetic including mass and heat transfer [18]. Therefore, modification of the model by incorporating correction factors is necessary for prediction of the actual gasification performance.

2.4.2. Modification of model

To further improve the model accuracy, the correction factors and hydrocarbon amount and composition are incorporated as a function of ER and temperature as shown in Figs. 2–5. With such modification, the model ability to predict syngas composition within the given ER and temperature range is enhanced. Regression analysis is conducted in Microsoft Excel to establish the relationships between the correction factors and hydrocarbon composition with ER and temperature. The findings are summarised in Table 4–7.

As shown in Figs. 2–5 and Table 4–7, correction factors and hydrocarbon composition and amount vary with temperature and ER,

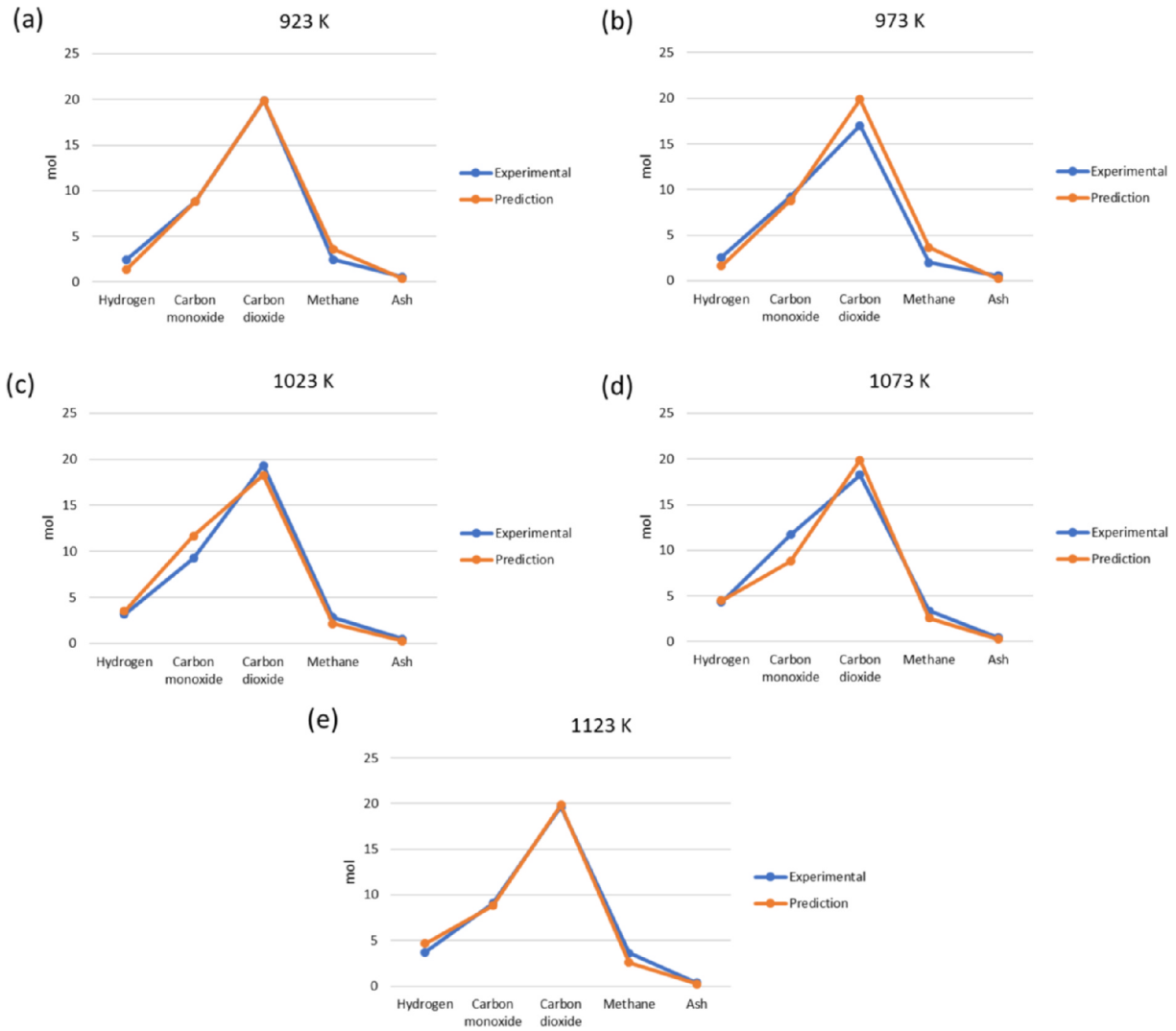


Fig. 7. Major components of syngas (H_2 , CO, CO_2 , and CH_4) and solid carbon (C) at a series of temperature as determined from experimental gasification of NG and model prediction.

which deviate from constant behaviour as reported in other works [5–7]. Since the reactions in gasifier are not in equilibrium conditions, the model is modified by multiplying equilibrium constants (Eqs. (12)–(17)) with correction factors (Eqs. (31)–(36)). There are twelve unknowns ($n_1 - n_8$, x , y , z , and p) but only 7 equations for each operating conditions (temperatures and ERs) (Eqs. (2)–(6) and Eqs. (12)–(17) are available. Phase rule is used in this equilibrium model development in order to determine the number of independent equilibrium reactions. The phase rule formula is presented in Eq. (47).

$$F = C - P + 2 \quad (47)$$

where F is the degree of freedom, C is the number of components, and P is the number of phases.

In this work, the number of components in the product stream is 12 and the number of phase is 3. Therefore, the degree of freedom for this system is 11. Hence, 11 constraints are required for a complete definition of the system. The constraints are temperature, ER, pressure, 4 atomic balances (C, H, N and O from the feedstocks) and 3 equilibrium constants with correction factors for each operating condition. Based on this analysis, an additional equation is needed to solve for coefficient of hydrocarbon residues, n_8 . Therefore, additional relationships between gas to hydrocarbon residues ratio (SR) with temperature and ER are introduced in the modified model. The correlations are depicted in Fig. 6. Regression analysis of the correlations is summarised in Table 8.

3. Model validation

Major components of syngas and solid carbon as determined from experimental gasification of NG and model prediction are presented in Fig. 7 and Fig. 8. RMS deviation between predicted and experimentally measured value is summarised in Table 9 and Table 10.

The high operating temperature provides favourable conditions for endothermic reversible steam methane reforming, water-gas and dry reforming reactions. The production of hydrogen is enhanced as the heat absorbing reactions shift the equilibrium to the right [20].

More oxygen is injected into the reactor at higher ER which in turn promotes CH_4 combustion with O_2 while retarding methanation reaction for CH_4 formation. As oxygen amount decreases at lower ER, the carbon converts into CO instead of CO_2 through oxidation and partial combustion reactions. As the amount of CO increased, more CH_4 and H_2 are formed through methanation and water-gas shift reactions. Hence, higher concentration of CH_4 and H_2 are detected in producer gas at lower ER [20].

It is noteworthy to mention that the accuracy of syngas and carbon prediction from this approach is higher compared to the previous research [10]. Based on previous research, the average RMS values are 0.247 for bagasse, 0.319 for rice husk, 0.452 for coconut shell and 0.306 for palm kernel shell.

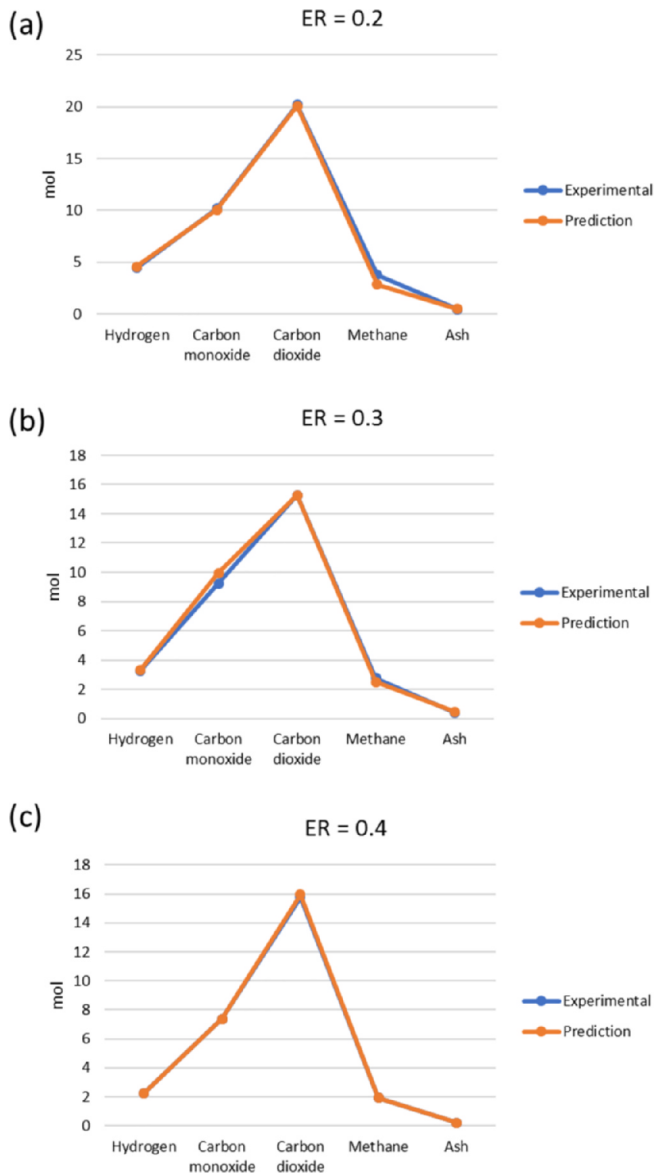


Fig. 8. Major components of syngas (H_2 , CO , CO_2 , and CH_4) and solid carbon (C) as determined from experimental gasification of NG and model prediction.

Table 9

RMS error of the model prediction at a series of ER (constant temperature of 1123 K).

ER	RMS
0.2	0.0155
0.3	0.051
0.4	0.0017
Average RMS	0.0227

4. Case study: optimisation of hydrogen production

Due to the good accuracy of syngas and carbon prediction by the model, the gasifier can be further optimised to achieve various objectives, for example, optimising H_2 production. Additional constraints are considered in the model due to limitations of gasifier available in the laboratory. In this study, the gasifier is fixed to be operated at an ambient pressure of 1 atm, a temperature range of 923 – 1123 K, and an ER range of 0.2 – 0.4. Hydrogen fuel has great potential as a clean fuel to

Table 10

RMS error of the model prediction at a series of temperature (constant ER of 0.25 K).

Temperature (K)	RMS
923	0.077
973	0.133
1023	0.114
1073	0.122
1123	0.108
Average RMS	0.1108

Table 11

Comparison of the model result prediction with experimental result in optimum operating condition.

Optimum T	1123 K	
Optimum ER	0.2092	
	Modified model	Experimental result
Mole basis (mol)		
H_2 , n_1	4.77	4.53
CO , n_2	7.84	11.26
CO_2 , n_3	20.19	17.36
CH_4 , n_5	1.94	2.29
Ash, n_7	0.5121	0.4633
RMS	0.0383	
Mass basis(g/kg biomass)		
H_2 , n_1	3.86	3.62
CO , n_2	87.81	126.11
CO_2 , n_3	355.34	305.54
CH_4 , n_5	12.42	14.66
Ash, n_7 (kg/kg)	0.25	0.22

replace fossil fuels to combat energy shortage issue in the future. Therefore, in this work, the optimisation objective is to maximise hydrogen, n_1 . As determined from the model, hydrogen production is maximised at ER of 0.2092 and temperature of 1123 K.

A comparison between the predicted and experimentally measured of syngas composition produced at optimised conditions is presented in Table 11. The experimental result showed a good agreement with the predicted data from the modified model. Nevertheless, some discrepancies are observed between predicted results and the experimental values for gas compositions. The modified model has slightly over-predicted the production of H_2 , CO_2 and ash generation and it under-predicted the composition of CO and CH_4 . RMS at the optimum operating condition is 0.0383, implying a reasonably accurate prediction by the model.

5. Conclusions

In this study, a stoichiometric equilibrium model is developed for simulation of air gasification of Napier grass. The model is modified to include correction factors at a series of temperatures and ERs which are multiplied with equilibrium constants to improve the accuracy of the model in predicting syngas and carbon compositions. The predicted values are in good agreement with experimental results, validating the model as a reliable tool for simulation of gasification performance. Average RMS values of 0.0227 and 0.1108 at a series of ER and temperature respectively imply that the model is able to simulate gasification performance with good accuracy. The modified model is further utilised to determine optimum operating conditions for maximum hydrogen production which are determined to be at ER of 0.2092 and operating temperature of 1123 K. As part for future works, the model will be further tested with a range of biomass feedstocks.

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CRediT authorship contribution statement

Mohamad Syazarudin Md Said: Data curation, Writing - original draft. **Wan Azlina Wan Ab Karim Ghani:** Conceptualization, Methodology. **Tan Hong Boon:** Visualization, Investigation. **Denny Ng Kok Sum:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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